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ISSN 0350-350X
GOMABN 39, 4, 229-244
Izvorni znanstveni rad/Original scientific paper
UDK 621.892.004.64 : 614.7 : 576.343 : 615.9 : 577.4

EKOLOŠKI PRIHVATLJIVA MAZIVA

Sažetak

Ekološki prihvatljiva maziva su ona, koja će u kontaktu s okolišem uzrokovati minimum štetnog djelovanja, i kod proizvodnje i primjene i kod zbrinjavanja otpada. Jedan od uvjeta ekološke prihvatljivosti je biološka razgradljivost maziva. Pored biološke razgradljivosti potrebna su i ekotoksikološka ispitivanja na bakterije, alge i ribe te određivanje bioakumulacije maziva.

1. UVOD

Posljednjih 20 godina raste interes za ekološki prihvatljivim mazivima kao zamjenom za mineralna ulja u područjima gdje pri primjeni mineralno ulje može izazvati štete u okolišu. To su npr. gubici ulja kod motornih pila, poljoprivrednih, šumarskih i građevinskih strojeva, željezničkih i tramvajskih skretnica i tračnica, izvanbrodskih motora, zatim ulja za kalupe u građevinarstvu gdje mazivo 100% ostaje u okolišu. Strategija proizvođača maziva usmjerava se na proizvodnju ekološki prihvatljivih maziva za što su i ustanovljeni kriteriji poput npr. "plavog anđela" u Njemačkoj, i druge oznake "zaštite okoliša". Tržište biorazgradljivim mazivima jest i ostat će za mnoge proizvođače tržište budućnosti [1].

Time se očekuje značajnije povećan udio biorazgradljivih maziva kod spomenutih primjena kod kojih postoji vjerojatnost i mogućnost prodiranja maziva u okoliš, tlo te površinske i podzemne vode.

Pod takvim uvjetima primjene gdje mazivo pri uporabi dospijeva u okoliš, važno je znati kakvo je njegovo ekotoksikološko djelovanje. To znači da li će to mazivo ili njegovi razgradni produkti promijeniti prirodna svojstva vode, tla, zraka, klime, životinja, biljaka i mikroorganizama [2] ili će prirodnim

putem, tj. biološkom razgradnjom opet nestati iz okoliša. Zato se moraju uzeti u obzir svi navedeni aspekti utjecaja maziva na okoliš od proizvodnje, preko primjene do zbrinjavanja otpada, kako bi se mogla opisati njihova ekološka podobnost [3]:

1. Proizvodnja maziva mora biti ekološki prihvatljiva, što znači mali utrošak energije, bez otpada i bez emisije.
2. Upotrijebiti po mogućnosti sirovine bez iscrpljivanja resursa i bez efekta staklenika.
3. Pri uporabi maziva moraju biti fiziološki opravdana, što znači nisu toksična, niti kancerogena, niti mutagena, niti teratogena.
4. Za vrijeme uporabe ne smiju nastati toksične tvari, dakle bez bioakumulacijskog potencijala.
5. Maziva moraju biti ekotoksikološki podnošljiva, znači da nisu štetna za vode, da se ne miješaju s vodom i da su lakša od vode.
6. Nakon uporabe moraju biti brzo biološki razgradljiva bez toksičnih i neugodnih razgradnih produkata.
7. Ne smiju stvarati probleme pri zbrinjavanju otpada tj. mora biti moguće jednostavno recikliranje.

2. ZAKONSKI PROPISI ZA ODREĐIVANJE BIOLOŠKE RAZGRADNJE I EKOTOKSIČNOSTI KOJI SE ODNOSE NA MAZIVA

2.1. Internacionalni propisi:

Na temelju smjernica Europske unije (EU) 67/548 za svrstavanje, pakiranje i označavanje opasnih tvari donesen je niz novih uputa u vezi ispitivanja opasnih tvari:

- 92/32/EU L 154 A od 05.06.1992. str. 1 (7. dodatak)
- 92/69/EU L 383 A od 29.12.1992. str. 11 (17. dodatak)
- 93/67/EU L 110 A od 04.05.1993. str. 68
- 93/67/EU L 227 A od 08.09.1993. str. 9
- L 73 od 16.03.1994. str. 2 (Helsinški dogovor o zaštiti mora)
- MARPOL 1973/78 s nadopunama 07.09.1984. i 05.12.1986. (Očuvanje mora od zagađenja brodovima)
- GESAMP (1989) The evaluation of the hazardous of harmful suptances carried by ships: Revision of GESAMP Reports and Studies No. 17 Rep. Stud. GESAMP 35

2.2. Nacionalni propisi:

- Zakon o vodama (NN br. 107 od 27.12.1995. član 132 i133)
- Zakon o zaštiti okoliša (NN br. 82 od 11.11.1994. član 24)
- Pravilnik o izdavanju vodopravnih akata (NN br. 28 od 12.04.1996. član 20 i 21)
- Pravilnik o graničnim vrijednostima pokazatelja, opasnih i drugih tvari u otpadnim vodama (NN br. 40 od 27.04.1999.)
- Sigurnosno tehnički list za kemijske proizvode HRN ISO 11014-1:1996:
- Točka 12 Ekološki podaci (Pokretljivost, postojanost/razgradljivost, bioakumulacija, učinci proizvoda na okoliš, ekotoksičnost)

3. BIOLOŠKA RAZGRADNJA

Biološka razgradnja je biološka pretvorba tvari ili smjese tvari pomoću mikroorganizama, uz ili bez prisutnosti kisika.

Prema OECD postoji podjela na: "ready biodegradability" (brza biološka razgradnja), "acceptable biodegradability" (dovoljna biološka razgradnja) i "inherent biodegradability" (inherentna biološka razgradnja).

Prema smjernicama Europske unije (OJ No L 383 A/221 od 29.12.1992.) i kriterijima ocjene biološke razgradnje koje propisuju također smjernice Europske unije (OJ No L 110A/70 od 04.05.1993.) postoje sljedeće definicije:

- primarna biološka razgradnja:
je promjena kemijske strukture ispitivane tvari, postignuta biološkom aktivnošću što rezultira gubitkom specifičnog svojstva te tvari.

- totalna biološka razgradnja (aerobna):
je stupanj ostvarene razgradnje kada mikroorganizmi potpuno razgrade ispitivanu tvar što rezultira stvaranjem ugljičnog dioksida, vode, mineralnih soli i biomase.

Prema kriterijima tvar je potpuno biološki razgradljiva ako u pokusu nakon **28** dana dostigne vrijednost stupnja razgradnje od 70% otopljenog organskog ugljika (DOC) ili 60% CO_2 ili 60% O_2.

- brza biološka razgradnja:
je ona razgradnja kod koje nakon što se postigne 10% razgradnje u daljnih 10 dana ("10-dnevni prozor") stupanj razgradnje dostigne vrijednost od 70% DOC, ili 60% CO_2, ili 60% O_2.

- inherentna biološka razgradnja:
je ona kod koje se koristi prethodno adaptirana kultura na ispitivanu tvar ili smjesu tvari u bilo kojem priznatom testu biološke razgradnje.

Kod biološke razgradnje maziva primarna biološka razgradnja prati smanjenje glavne komponente, tj. ulja odgovarajućom metodom (npr. infracrvenom spektrometrijom ili plinskom kromatografijom), dok se kod totalne biološke razgradnje mjeri nastali CO_2 također odgovarajućim metodama. Jedino totalna biološka razgradnja daje pravu informaciju da li se mazivo potpuno razgradilo do CO_2 i vode.

Odabir metode za određivanje biološke razgradnje ovisi o svojstvima i sastavu maziva. U tablici 1 navedene su metode za određivanje biološke razgradnje propisane Službenim listom Europske unije i ISO norme izdane od Internacionalne organizacije za standardizaciju, a koje za sada i službeno prihvaća Republika Hrvatska.

Tablica 1: Metode za određivanje biološke razgradnje
Table 1: Biodegradability determination methods

Naziv metode/Name of Method	EU[1]	ISO[2]	OECD[3]	Mjerni parametri
DOC Die-away Test	C4A	7827	301A	DOC[4]
Modificirani OECD Screnning Test	C4B	7827	301E	DOC
Modificirani Sturm Test	C4C	9439	301B	CO_2
Manometrijski respiracijski test/Manometric Respiration Test	C4D	9408	301F	BPK[5]
Test zatvorenih bočica/Closed Bottles Test	C4E	10707	301D	BPK
MITI- Test	C4F		301C	BPK
Modificirani SCAS Test	-	9887	302A	DOC
Zahn-Wellens Test/ EMPA Test	-	9888	302B	DOC
Modificirani MITI Test (II)	-	-	302C	BPK
Aerobni tretman otpadnih voda/Aerobic Wastewater Treatment	-	11733	303	DOC
Inherentna biorazgradnja u tlu/Inherent Soil Biodegradability	-	-	304	
Biološka razgradnja morske vode/Sea Water Biodegradability	-	-	306	
Upute za pripremu teško topljivih tvari u vodi za određivanje biološke razgradnje/Instructions for Preparing Water-Resistant Substances for Biodegradability Determination	-	10634	-	-
Anaerobni degradacijski test	-	11734	-	DIC
Test zatvorenih bočica- dvije faze/Closed Bottles Test - Two Phases	-	10708	-	BPK
Biodegradacijski test kod niskih koncentracija/Low Concentration Biodegradability Test	-	14592	-	-
CO_2 test u "zataljenim" bočicama/CO_2 Test in "Sealed" Bottles	-	14593	-	CO_2

[1]) Europska unija (EU)
[2]) Internacionalna organizacija za standardizaciju (ISO)
[3]) Organizacija za ekonomsku suradnju i razvoj (OECD)
[4]) Otopljeni organski ugljik (dissolvend organic carbon) (DOC)= Dissolved Organic Carbon (DOC)
[5]) Biološka potrošnja kisika (BPK)= Biological Oxygen Consumption (BOC (orig. abbrev.: BPK)

Sve su ove metode ponajprije namijenjene za određivanje biološke razgradnje kemijskih tvari koje su vodotopljive, kemijski stabilne i nisu komplesnog sastava. Međutim, maziva su upravo kompleksne smjese ugljikovodika s vrlo malom vodotopljivošću pa ih je potrebno prethodno pripremiti prema uputi opisanoj u ISO 10634 i ISO 10708. Na taj se način dobiju emulzije ili disperzije maziva čija se biološka razgradnja provodi u vodenom mediju. Međutim, pokusi su dokazali [4,5,10.] da direktno dodavanje maziva u mineralni medij, tj. vodenu otopinu soli s bakterijskom kulturom, daje bolje rezultate nego kada je mazivo prethodno emulgirano ili dispergirano. Potrebno je kontinuirano miješanje tako direktno dodanog maziva tijekom 28 dana koliko u pravilu traje pokus biološke razgradnje. Modificiranom Sturm metodom (EU C4C ili ISO 9439) pri tome se izravno prati nastali CO_2 kao produkt potpune razgradnje maziva. Ova je metoda poslužila kao osnova za novu metodu (CO_2 headspace test) za određivanje totalne biološke razgradnje praćenjem nastalog CO_2 u "zataljenim" bočicama.

Do sada je najviše upotrebljavana metoda za određivanje biološke razgradnje maziva bila CEC–L–33–A–83 metoda [7]. Ovu je analitičku metodu razvio Swiss Federal Establishment for Testing Materials za određivanje biološke razgradnje ulja koja se koriste u dvotaktnim izvanbrodskim motorima. S obzirom da ova metoda prati primarnu biološku razgradnju, tj. samo smanjenje koncentracije ulja, sve se više zamjenjuje metodama koje daju podatak o totalnoj biološkoj razgradnji do CO_2 i vode.

CONCAWE (The oil companies' european organization for environment, health and safety) je u novije vrijeme razradila i objavila novu metodu za određivanje inherentne biološke razgradnje maziva ("A test method to assess the 'inherent' biodegradability of oil products" report no. 99/59). Ova je metoda kompatibilna s ISO 14593 Water quality - Evaluation of ultimate aerobic biodegradability of organic compounds in aqueous medium - Method by analysis of inorganic carbon in sealed vessels (CO_2 headspace test), uz razliku, što koristi prethodno adaptiranu kulturu na ispitivano mazivo.

Izvješće o ispitivanju biološke razgradnje maziva mora sadržavati podatke o zadovoljavanju uvjeta koje zahtijeva metoda ispitivanja, a to su:

- kemijski naziv za sastojke maziva i referentne tvari; podatak o njihovoj čistoći;
- uvjeti pokusa;
- cjepivo: izvor, koncentracija i postupak pripreme;
- trajanje pokusa i temperatura;

- način pripreme maziva za pokus;
- primijenjena metoda: navesti svaku promjenu postupka u odnosu na standardni postupak uz obrazloženje;
- prikaz rezultata;
- podatke o inhibiciji;
- podatke o abiotskoj razgradnji;
- podatke o specifičnim kemijskim analizama (ako su dostupni);
- grafički prikaz postotka razgradnje tijekom pokusa za mazivo i referentnu tvar; naznačiti fazu suzdržanog rasta, fazu razgradnje i 10-dnevno razdoblje; ukoliko je pokus zadovoljio kriterije valjanosti, u grafički prikaz se unosi prosječna vrijednost postotka razgradnje od dva određivanja;
- postotak razgradnje nakon 10-dnevnog razdoblja i nakon postignuća konstantne razgradnje, te na kraju pokusa.

4. EKOTOKSIKOLOŠKA ISPITIVANJA – AKVATIČKI TOKSICITET

Toksicitet je toksično djelovanje tvari ili smjese tvari na živi organizam (npr. bakterije, alge, ribe, sisavce). Ispitivanjem toksičnosti pojedinih model organizama ocjenjuje se toksičnost tvari na biocenozu i označava kao ekotoksicitet. Najčešća ispitivanja toksičnosti rade se testovima na vodene organizme: alge, vrsti *Daphnia magna* i ribe. Metode ispitivanja odnose se na akutnu toksičnost, produljenu toksičnost, na ispitivanje djelovanja na nasljednu tvar DNA (genotoksicitet i mutageneza), djelovanje na cjelokupni organizam ili naknadno djelovanje na više organizme u biocenozi. Za ispitivanja akutne i produljene toksičnosti propisane metode od OECD, EU i ISO odnose se na tvari koje su vodotopljive, kemijski stabilne, nehlapljive i koje nisu kompleksnog sastava. Za maziva koja spadaju u vodonetopljive, kompleksne smjese, potrebno je ove metode doraditi prethodnom obradom uzorka. Za sada najbolja raspoloživa metoda pripreme maziva za ispitivanje toksičnosti na vodene organizme je WAF metodologija (Water Accomodated Fraction). WAF predstavlja vodeni medij koji sadrži onu frakciju proizvoda koja ostaje u vodenoj fazi nakon miješanja i vremenskog razdoblja za odvajanje faza [6,8,9]. To znači, da se toksičnost maziva na vodene organizme odnosi samo na onu koncentraciju maziva koja se pod određenim uvjetima otopila u vodi, a ne kompletno mazivo koje je na taj organizam na drugi način djelovalo npr. mehanički, obljepljivanjem. Upravo su izlijevanja sirove nafte u vodu potaknula istraživanja toksičnosti na vodene organizme i osnova su za ocjenu toksičnosti i razvoj međunarodnih zakonskih regulativa za kemijske proizvode, posebno za proizvode naftne industrije.

Rezultati laboratorijskih ispitivanja izraženi su preko vrijednosti efektivne koncentracije (EC) i letalne koncentracije (LC).

Efektivna koncentracija (EC) je brojčana veličina za djelovanje tvari određene koncentracije kod koje je promatrano određeno djelovanje. Npr., EC_{50} označava koncentraciju kod koje je bilo promatrano djelovanje na 50% test životinja koje su bile usmrćene ili imobilizirane, te se u slučaju mortaliteta označavaju i kao letalna koncentracija.

EC_0 je najviša ispitivana koncentracija kod koje nema djelovanja
(LC_0: svi organizmi su preživjeli)

EC_{50} je koncentracija kod koje dolazi do djelovanja na 50% test organizama
(LC_{50}: 50% organizama je uginulo)

EC_{100} je najniža koncentracija kod koje dolazi do djelovanja na 100% organizama
(LC_{100}: svi organizmi su uginuli)

Izvješće o ispitivanju toksičnosti maziva na vodene organizme mora sadržavati sljedeće podatke, a to su:

- podatak o indikatorskom organizmu (točan naziv, vrsta, podrijetlo, prethodni tretman, metoda uzgoja – uključujući izvor, vrstu i količinu hrane, učestalost hranjenja);
- izvor vode za razrjeđivanje i njezine osnovne fizičko-kemijske osobine (npr. pH, temperatura, tvrdoća);
- navesti metodu pripreme maziva za ispitivanje;
- koncentracija pomoćne tvari ukoliko je upotrijebljena;
- popis upotrijebljenih koncentracija određivanog maziva i dostupne podatke o njihovoj stabilnosti;
- ukoliko je tijekom pokusa određivana koncentracija otopina, navesti upotrijebljene metode i postignute rezultate;
- opis opreme za ispitivanje;
- koncentracija otopljenog kisika; vrijednost pH i temperature ispitivanih otopina;
- dokaz da su bili zadovoljeni kriteriji kvalitete;
- tabelarni i grafički prikaz rezultata za svako vrijeme promatranja;
- navesti vrijednost EC_{50} za svako vrijeme promatranja s granicama pouzdanosti od 95%;
- statističke postupke upotrijebljene pri određivanju vrijednosti EC_{50};
- ukoliko je ispitivana referentna tvar, navesti postignute rezultate;
- najviša koncentracija određivanog maziva kod koje nema djelovanja;

– najniža koncentracija određivanog maziva kod koje je došlo do 100%-tnog djelovanja na organizme.

Kriteriji ocjene akvatičkog toksiciteta prema smjernicama Europske unije (OJ No L 110A od 04.05.1993.):

– vrlo toksično: $EC_{50} \leq 1$ mg/l
– toksično: 1 mg/l < $EC_{50} \leq 10$ mg/l
– štetno: 10 mg/l < $EC_{50} \leq 100$ mg/l

Ove kriterije treba nadopuniti daljnjim ispitivanjima toksičnosti koja se odnose na produljeno vrijeme ispitivanja, dinamiku i kinetiku, biološku razgradnju i bioakumulaciju, lokalno djelovanje otrova, ovisnost o biotičim i abiotičkim uvjetima (temperatura, prehrana...).

5. ZAKLJUČAK

Uz saznanje da samo 3% vode na Zemlji otpada na slatku vodu od čega prema današnjim tehničkim mogućnostima na pitku vodu otpada 3,6 mil. km^3, tj. svega 0,27% od ukupne količine vode, potrebno je voditi brigu da se koriste ekološki prihvatljiva maziva ako želimo očuvati prirodnu čistu i bistru vodu koja je uvjet opstanka života na Zemlji.

Veću tržišnu cijenu ekološki prihvatljivih maziva potrebno je prihvatiti u cilju očuvanja neprocjenjive vrijednosti čistog okoliša. Da je mazivo doista ekološki prihvatljivo, potrebno je dokazati nizom ispitivanja, kao: biološkom razgradnjom tijekom 28 dana, pokusima ekotoksičnosti i bioakumulacije te po potrebi i specijalnim ispitivanjima, npr. ispitivanje utjecaja prisutnosti teških metala koji svojim djelovanjem opterećuju tlo i vodu.

Da bi se mogli zadovoljiti opsežni uvjeti procjene ekološke prihvatljivosti maziva, potrebno je odabrati prave metode ispitivanja poznavajući sastav i svojstva maziva.

ENVIRONMENTALLY TOLERABLE LUBRICANTS

Abstract

Ecologically acceptable lubricants are those that when in contact with the environment cause minimal detrimental effects, both in the process of production and application as well as in the phase of waste disposal. The biodegradability of lubricants is one of the conditions of their ecological acceptability. Along with the biodegradability condition, an ecotoxicological testing on bacterias, sea weeds (algae) and fish is necessary to determine the bioaccumulation of lubricants.

1. INTRODUCTION

Over the past 20 years, the interest has grown into environmentally tolerable lubricants as a replacement for mineral oils in applications where the latter may cause damage to the environment. These are, for instance, oil losses in the use of chain saws, agricultural, forestry, and construction machinery, railway and tram switches and tracks, outboard engines, as well as oils for concrete moulds, where 100% of the lubricant remains in the environment. The strategy of lubricant manufacturers is oriented towards the production of environmentally tolerable lubricants. Criteria such as the "Blue Angel" in Germany, as well as other "environmentally friendly" labels have been established for the purpose. The market of biodegradable lubricants remains for many manufacturers the market of the future /1/.

That is why we may expect an increase in the share of biodegradable lubricants for the aforementioned applications where there is both the probability and the possibility of the lubricant ending up in the environment, soil, as well as surface and underground waters.

Under such conditions, where the lubricant ends up in the environment during its use, it is important to know its ecotoxicological impact. This means: Whether the lubricant or its degradation products shall change the natural properties of water, soil, air, climate, animals, plants and microorganisms /2/ or will it disappear from the environment in a natural way i.e. through biodegradation. That is why it is necessary to take into account all of the aforementioned aspects of the lubricants' environmental

impact - from production, through application, to waste disposal, in order to be able to describe their environmental tolerability /3/:

1. Lubricant production has to be environmentally tolerable, which means low energy consumption, no waste, and no emission.
2. The feeds used should preferably avoid resource exploitation and greenhouse effect.
3. At use, the lubricants have to be physiologically justified, which means non-toxic, non-cancerogenic, non-mutagenic, and non-teratogenic.
4. Their use must not result in the generation of toxic substances, which means that they have to be deprived of any bioaccumulative potential.
5. The lubricants must be ecotoxicologically tolerable, meaning that they are not water-hazardous or water-miscible, and that they are lighter than water.
6. After use, they must be readily biodegradable, without toxic or any other unpleasant degradation products.
7. They must not cause any problems for waste management, which requires their easy recycling.

2. LEGAL REGULATIONS FOR DETERMINING LUBRICANT BIODEGRADABILITY AND ECOTOXICITY

2.1. International Regulations

Based on the EU Guidelines 67/548 for the classification, packaging, and labelling of harmful substances, a series of new Instructions has been passed with regard to the testing of harmful substances:

- 92/32/EU L 154 A of 5 June, 1992, p. 1 (Adendum 7)
- 92/69/EU L 383 A of 29 Dec., 1992, p. 11 (Adendum 17)
- 93/67/EU L 110 A of 4 May, 1993, p. 68
- 93/67/EU L 227 A of 8 Sept., 1993, p. 9
- L 73 of 16 March, 1994, p. 2 (The Helsinki Agreement on Sea Protection)
- MARPOL 1973/78, ammended on 7 Sept., 1984 and 5 Dec., 1986 (Sea Protection Against Pollution by Ships)
- GESAMP (1989) The evaluation of the hazards of harmful substances carried by ships: Revision of GESAMP Reports and Studies No 17 Rep. Stud. GESAMP 35

2.2. National Regulations:

- The Waters Act (NN No 107 of 27 Dec. 1995, Articles 132 and 133)
- The Environmental Protection Act (NN No 82 of 11 Nov. 1994, Article 24)

- The Book of Rules on the Issuing of Water-related Legal Documents (NN No 28 of 12 Apr. 1996, Articles 20 and 21)
- The Book of Rules on the Limit Values of Indicators, Harmful and Other Substances in Wastewaters (NN No 40 of 27 Apr. 1999)
- The Technical Safety Sheet for Chemical Products HRN ISO 11014-1:1996: Clause 12 Environmental Data (movability, persistence/ biodegradability, bioaccumulation, the product's environmental impacts, ecotoxicity)

3. BIODEGRADABILITY

Biodegradability is the biological transformation of a substance or a compound of substances by means of microogranisms, with or without the presence of oxygen.

According to OECD, it is classified into ready, acceptable, and inherent biodegradability.

According to the EU Guidelines (OJ No L 383 A/221 of 29 Dec., 1992), and the criteria for biodegradability evaluation, also set by the EU Guidelines (OJ No L 110 A/70 of 4 May., 1993), there exist the following definitions:

***- primary biodegradability*:**
is a change in the chemical structure of the substance tested, achieved through biological activity and resulting in the loss of the substance's specific property.

***- total biodegradability (aerobic)*:**
is the degree of achieved degradation when the microorganisms completely degrade the substance tested, resulting in the generation of carbon dioxide, water, mineral salts, and biomass.
According to the criteria set, a substance is completely biodegradable if in a test lasting 28 days it achieves the degradation degree value of 70% DOC-dissolved organic carbon, or 60% CO_2, or 60% O_2.

***- ready biodegradability*:**
is the degradation which, having achieved 10% of degradation, reaches the value of 70% DOC, or 60% CO_2, or 60% O_2 within the next 10 days (the so called "10-day window").

***- inherent biodegradability*:**
is the one using a culture that has been previously adapted to the tested substance or compound in any of the recognized biodegradability tests.

In the biodegradability of lubricants, the primary biodegradability follows the lowering of the main component i.e. oil by a corresponding method e.g. infrared spectrometry of gas chromatography, while, in the case of total

biodegradability, the generated CO_2 is being measured, also by appropriate methods. Only the total biodegradability provides an accurate information on whether a lubricant has been completely degraded into CO_2 and water.

The choice of the method for biodegradability determination depends on the lubricant properties and composition. Table 1 lists biodegradability determination methods prescribed by the EU Official Gazette and ISO standards issued by the International Standardization Organization, for the time being officialy adopted by the Republic of Croatia as well. (Table 1).

All these methods are intended primarily for determining the biodegradability of water-soluble and stable chemical substances which do not have a complex composition. However, lubricants constitute complex hydrocarbon compounds with very low water-solubility level, which is why they first have to be prepared according to the instruction described in ISO 10634 and ISO 10708. In this manner we obtain lubricant emulsions or dispersions whose biodegradation then proceeds in an aqueous medium. However, tests have shown /4,5,10/ that a direct adding of lubricant into the mineral medium i.e. water saline solution with a bacterial culture provides better results than when the lubricant is first emulsified or dispersed. Such a directly added medium requires continuous mixing during the 28 days of the usual biodegradability test duration. The Modified Sturm Method (EU C4C or ISO 9439) directly monitors CO_2 generated as a product of complete lubricant degradation. This method has served as the basis of a new method (CO_2 headspace test) for determining total biodegradability by monitoring the CO_2 generated in "sealed" bottles.

The most frequently used method for lubricant biodegradability determination has so far been the CEC-L-33-A-83 method /7/. This analytical method has been elaborated by the Swiss Federal Establishment for Testing Materials, for determining the biodegradability of oils used in two-stroke outboard engines. Since the said method monitors primary biodegradability i.e. only the oil concentration lowering, it is being increasingly replaced by methods providing information on total biodegradability into CO_2 and water. CONCAWE (The Oil Companies' European Organization for Environment, Health and Safety) has recently elaborated and published a new Test method to assess the 'inherent' biodegradability of oil products, report no. 99/59. This method is compatible with ISO 14593 Water quality - evaluation of ultimate aerobic biodegradability of organic compounds in aqueous medium - Method by analysis of inorganic carbon in sealed vessels (CO_2 headspace

test), the only difference being that it uses the culture that has previously been adapted to the tested lubricant.

The report on lubricant biodegradability testing must contain information on the meeting of conditions required by the test method, as follows:

- chemical name for lubricant components and referential substances; information on their purity;
- test conditions;
- vaccine: source, concentration, and preparation procedure;
- test duration and temperature;
- the manner of lubricant preparation for the test;
- the method applied, stating and explaining every change with regard to standard procedure;
- presentation of results;
- data on inhibition;
- data on abiotic degradation;
- data on specific chemical analyses (if available);
- graphical presentation of degradation percentage during the test for both the lubricant and the referential substance, specifying the restrained growth phase, the degradation phase, and the 10-day period. If the test has met with the validity criteria, the graphical presentation includes also the average degradation percentage value calculated on the basis of two measurements;
- degradation percentage after the 10-day period, as well as after constant degradation has been achieved, and at the end of the test.

4. ECOTOXIC TESTS - AQUATIC TOXICITY

Toxicity is the toxic impact of a substance or a compound on the living organism (i.e. bacteria, algae, fish, mammals). By testing the ecotoxicity of given model organisms, the substance's biocenosis toxicity is being determined and identified as ecotoxicity. Toxicity tests are most freqently done with water organisms: Algae of the *Daphnia magna* species and fish. The test methods refer to acute toxicity, prolonged toxicity; testing the impact on the DNA genetic substance (genotoxicity and mutagenesis); impact on the entire organism or subsequent impact on higher organisms in biocenosis. The methods prescribed on the part of OECD, EU and ISO for testing acute and prolonged toxicity refer to water-soluble, chemically stable, non-volatile substances, of non-complex composition. Lubricants, pertaining to water-insoluble and complex compounds require an addition to these methods through previous sample treatment. The best method available at the moment

for lubricant preparation in view of testing their aquatic toxicity is the WAF (Water Accommodated Fraction) methodology. WAF constitutes an aqueous medium containing that fraction of the product which remains in the aqueous phase after mixing and after the phase separation period /6,8,9/. This means that lubricant aquatic toxicity refers only to that lubricant concentration which has under certain conditions dissolved in water, and not to the entire lubricant that may have had a different impact on that particular organism - e.g. mechanical, by sticking. Crude oil spills into water have been the ones to encourage aquatic toxicity tests. They constitute the basis for evaluating toxicity and elaborating international legal regulations for chemical products in general and oil industry products in particular.

The results of laboratory tests are expressed in terms of effective concentration (EC) and lethal concentration (LC).

Effective concentration (EC) is the numerical value for the impact of a substance in a given concentration for which a certain impact has been observed. E.g. EC_{50} describes concentration for which the impact has been observed on 50% of test animals that have been either killed or rendered immobile. In the case of their death, it is marked as lethal concentration.

EC_0 is the highest concentration tested which has had no impacts whatsoever (LC_0): All the organisms have survived)

EC_{50} is the concentration having impacted 50% of the test organisms (LC_{50}: 50% of the organisms have died)

EC_{100} is the lowest concentration impacting 100% of the organisms (LC_{100}: all of the organisms have died)

The report on testing lubricant aquatic toxicity must contain the data:

- information on the indicator organism (the exact name, species, origin, previous treatment, breeding method - including the source, type, and quantity of food, as well as feeding frequency);
- the source of water used for solution and its basic physico-chemical properties (e.g. pH, temperature, hardness);
- the method of lubricant preparation for the test;
- concentration of auxiliary substance, if used;
- the list of the lubricant concentrations used and the available data on their stability;
- if solution concentration has been determined during the test, specify the methods used and the results obtained;
- description of the test equipment;

- dissolved oxygen concentration; pH-value and temperature of the solutions tested;
- the proof that the quality criteria have been met;
- tabular and graphical presentation of results for every observation time;
- EC_{50} value for every observation time within 95% reliability limits;
- statistical procedures used when determining EC_{50} value;
- if referential substance has been tested as well, state the results achieved;
- the highest concentration of the tested lubricant without any impact whatsoever;
- the lowest concentration of the tested lubricant with a 100% impact on the organisms.

Criteria for evaluating acquatic toxicity in compliance with the EU Guidelines (OJ No L 110A of 4 May, 1993):

- very toxic: $EC_{50} \leq 1$ mg/l
- toxic: 1 mg/l$<EC_{50} \leq 10$ mg/l
- harmful: 10 mg/l$<EC_{50} \leq 100$ mg/l

These criteria need to be completed through further toxicity tests referring to prolonged testing time, dynamics and kinetics, biodegradability and bioaccummulation, poison impact, dependence on biotic and abiotic conditions (temperature, food...).

5. CONCLUSION

Given the realization that only 3% of the water on Earth refers to fresh water, out of which - according to the current technical possibilities - only 3.6 mil km^3 i.e. only 0.27% of the total water quantity refers to potable water, we must take care to use environmentally tolerable lubricants, if we wish to preserve naturally clean and clear water without which there is no survival on Earth.

The higher market price of environmentally tolerable lubricants must be accepted in order to preserve the immeasurably precious clean environment. The actual environmental tolerability of a lubricant must be proven by a series of tests, such as: Biodegradability in the course of 28 days, ecotoxicity and bioaccumulation tests, and, if necessary, special tests, e.g. testing the presence of heavy metals burdening both soil and water with their presence.

In order to meet the complex conditions of evaluating the environmental tolerability of lubricants, it is necessary to choose the right test methods, based on the lubricants' composition and properties.

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ključne riječi:	key words:
621.892.004.64 ekološka prihvatljivost maziva	ecological acceptability of lubricants
614.7 zagađivanje i zaštita okoliša	environment pollution and protection
576.343 biorazgradljivost	biodegradability
615.9 toksičnost	toxicity
577.4 ekosustav	ecosystem

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Primljeno/Received:

01.9.2000.